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Naval Ammunition Depot
Crane, Indiana

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The Navy has about 470 gross tons of red phosphorus smoke devices awaiting disposal. This paper reports on the ingredients of red phosphorus pyrotechnic compositions in these devices. Methods described are (a) total digestion, (b) acid extraction, (c) differential settling, (d) sublimation. and (e) incineration.

Total digestion methods yielded a solution which, when neutralized with ammonium hydroxide, was found to rank favorably with commercial nitrogen and phosphorus fertilizers.

Extraction of the metals from hot hydrochloric acid or with a mixture of sulfuric and oxalic acids allowed the recovery of 90% of the red phosphorus in elemental form at 90-95% purity. The experiments to sublime the red phosphorus directly from the composition were unsuccessful because of the formation of white phosphorus. The differential settling rate method did not prove acceptable.

In the incineration tests, up to 40% of the phosphorus from the pyrotechnic composition was recovered as phosphorus pentoxide; the balance remained in the residue as a mixture of phosphorus pentoxide and metal phosphates. The latter were difficult to remove even under the most stringent of conditions.

Total digestion, acid extraction (sulfuric and oxalic acids) and the incineration processes were analyzed on a cost effectiveness basis. The incineration process was the most effective.

PREFACE

The authors wish to acknowledge the support of Dr. Eldon Hood of Purdue University for conducting the soil additive experiment and for a comprehensive report of the findings.

The cooperation we received from SPCC (Mr. Grammer and Mr. Mizdial) and from NAD Crane (Mr. L. Shute) for supplying good inventory data of Condition Code H and ownership Code 2 items made the data in this report meaningful.

Also, we thank Mr. James Short and Ms. Karen Whorall for making the engineering cost calculations to determine the cost effectiveness of each process.

Mr. James Short also supplied the information from Battelle: Evaluation of the Design Concept for a Red Phosphorus Composition Incinerator.

Also, the authors wish to thank Dr. Kenneth A. Musselman for the initial work which established the dilution parameters for the nitric acid digestion method. These dilution parameters established the hypergolicity of the mixture if the nitric acid concentration exceeded 45%.

IMPORTANT COMMENT

In this work, we explored a large number of different methods concurrently. The reader will notice that some of the investigations were discontinued before all determinations about a given method were complete. The reason for this is simple. We discontinued work on a given method when it became apparent that another method would be more advantageous to the Navy. This is why some of the method developments described herein appear to be incomplete.

As the reader progresses through the report, he will realize that most of the effort was directed toward the nitric acid total digestion method, acid extraction, and controlled incineration. These methods turned out to be the most promising and are the ones which eventually were considered in the final analysis.

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INTRODUCTION

Currently, the Navy has about 470 gross tons of red phosphorus smoke devices awaiting disposal. A list of these items is in Appendix A. There are about 165000 units (individual devices) in a condition category of other than serviceable. It is estimated that there are about 160 tons of red phosphorus composition in these devices which needs to be processed for reclamation or disposal. Consequently, an investigation was made to find the cost effective methods for reclaiming or disposing of red phosphorus compositions in a safe, ecologically-permissible manner. This is a report of that work.

A typical formula for a pyrotechnic smoke composition containing red phosphorus is:

Ingredients	Weight Percent
Red Phosphorus - - - - - - -	53
Pyrolusite (MnO_2) - - - - -	34
Magnesium - - - - - - - - - -	7
Zinc Oxide - - - - - - - - - -	3
Linseed Oil - - - - - - - - -	3
	100

Compositions of this type either are generated as scrap material from a production operation or come from candles derived from deteriorated devices. In either case, we considered processes which might be used to dispose of the composition.

We will discuss the five alternate methods for reclamation/disposal of red phosphorus compositions. They are

1. Total Digestion Methods:
   a. Hot Nitric
   b. Wet Air Oxidation
2. Acid Extraction
   a. Sulfuric-oxalic
   b. Hot Hydrochloric
3. Differential Settling
4. Sublimation
5. Incineration.

TOTAL DIGESTION METHODS

The goal of these methods was to completely dissolve (digest) the red phosphorus composition in an acid solution, neutralize the solution, and use the resultant mixture as a soil additive. The two methods considered were nitric acid digestion and wet air oxidation. Their description follows.

Nitric Acid Digestion

Samples of smoke composition, consisting of red phosphorus, magnesium, manganese dioxide, zinc oxide and linseed oil, were digested with 35% nitric acid for one hour at 105°C. After removal of the 2% residue by filtration, the solution was neutralized with ammonium hydroxide which caused phosphate salts of magnesium, manganese, and zinc to precipitate.

This process produces a solution which, when adjusted to pH8 using concentrated ammonium hydroxide solution, provides a soil additive solution which contains approximately 4.4% P_4O_{10} (phosphoric anhydride) and 1.8% N_2 (soluble nitrogen), and 2% N_2 (insoluble nitrogen tied up in the metal ammonium phosphates) as well as the metallic ions of manganese (0.8%), magnesium (0.25%) and zinc (0.1%). This solution was tested by Purdue University agronomists as a soil additive on the Purdue University fescue grass and alfalfa farm.

The details of this digestion method are reported in reference 1. There was, however, an interesting observation made that is worthy of repeating here inasmuch as it bears directly on the process safety and pilot plant design, should this method be adopted. Two phenomena were observed for the reaction of red phosphorus smoke composition with nitric acid, varied from 10% to 70%.

1. No reaction occurred when less than 20% acid was utilized.

2. A hypergolic reaction resulted when concentrations exceeding 45% acid were used. Here, hypergolic is used to mean spontaneous ignition upon contact between the acid and the red phosphorus smoke composition.

This latter phenomena was pursued further, both in the library and the laboratory, in an attempt to identify what mixture of chemical ingredients, if any, was required to produce this result. We quickly observed that the combination of red

phosphorus and magnesium with concentrated nitric acid produced the hypergolicity. This was the only combination in which a hypergolic reaction was observed indicating that possibly a Group II-Group V metal mixture in the presence of a highly oxidizing acid may produce a hypergolic reaction. As yet, nothing has been turned up in the literature which alludes to a hypergolic reaction between red phosphorus and a Group II metal in the presence of concentrated nitric acid.

The red phosphorus-magnesium-nitric acid reaction was pursued in more depth. This reaction was observed to occur with both stabilized (aluminized) and technical (non-stabilized) red phosphorus. Of course the stabilized material could withstand a higher concentration of acid (viz., 55% vs 45%) before hypergolicity was initiated; however, once initiated, it proceeded with the same vigor and intensity that was observed with the technical grade red phosphorus.

The impact of this information is that the digestion process must be conducted using nitric acid concentrations of less than 45% and more than 20%. To control the acid concentration between these limits in the pilot plant would not be difficult.

The use of the solution resulting from this process as a soil additive is being evaluated as mentioned previously. The report of the first year's study is in reference 2. The solution was applied to tall fescue sod and to alfalfa plots. On a scale of 1 to 10, (10 being the best) the solution was compared to commercially available fertilizers. The solution is rated 8 as a phosphorus source and 9 as a nitrogen source.

The soil additive investigation over the first year indicates that waste red phosphorus pyrotechnic compositions can be converted into a useful soil additive. Plant tissue and soil analyses show that uptake of nitrogen and minerals from this inorganic additive is comparable to the commercial test fertilizer, triple superphosphate. However, it is necessary to look at the residual effect, i.e., second year growth as a function of all the first year variables, application rates, periodic uptake, leaching properties of the metal cations into the soil, and soil pH, and soil depletion. Therefore, the study will be continued for an additional growing season with monitoring and sampling at comparable periods as the first year.

The disadvantages of the nitric acid method are:

1. No separation of the materials is achieved.

2. Hot concentrated nitric acid is hazardous.

3. It is more expensive than the incineration process.

At the end of this report, the economic advantages of the nitric acid digestion method will be compared to the other methods that we considered.

Wet Air Oxidation

A wet air oxidation process[3] involving controlled oxidation of pea-sized chunks of red phosphorus smoke composition under 1600 psig and 230°C in 1% H_2SO_4 solution in a laboratory size autoclave was investigated at NSWC, Indian Head, Maryland location. The results of this process were a highly acidic solution and about 1-2 percent insoluble residue. Possibly this solution could be neutralized with ammonium hydroxide and used as a soil additive in a manner similar to the solution described above which resulted from nitric acid digestion and neutralization. No further work effort was expended on this method since the nitric acid method and controlled incineration seemed more promising at the time.

ACID EXTRACTION

Through this process we planned to recover the elemental phosphorus by removing the metals and metal oxides with acids. If in addition, the MnO_2 could be removed in a separate step, it too could be reclaimed. We also hoped to achieve a separation of some of the metals, in particular manganese, from the others, i.e., Mg, Zn, and Fe.

The basic difficulty was dissolving the mineral grade pyrolusite (MnO_2) without attacking the phosphorus. Since there were a number of acids which were promising for this purpose, and a variety of methods were possible, we limited our investigation to two variations. These are:

1. Extraction of manganese with oxalic acid, and

2. Extraction of manganese with hydrochloric acid.

A summary of these methods follows.

Extraction with Oxalic Acid

The basic reaction is the reduction of manganese dioxide with oxalic acid in the presence of acid:

$$MnO_2 + (COOH)_2 + 2H^+ \rightarrow Mn^{++} + 2CO_2\uparrow + 2H_2O.$$

First it was desired to remove the magnesium and the zinc oxide. Two weighed samples ~5g each of the original smoke comp were heated in an excess of warm dilute acid for three hours at about 80°C. Sulfuric acid was employed for Sample No. 1 and nitric acid for Sample No. 2.

Although some reaction was still occurring at the end of this period, the samples were filtered. The filtrates were found to contain the following percentages of the materials assumed to have been initially present:

	P	MnO_2	Mg	ZnO	Fe_2O_3
Sample No. 1	0	8%	92%	63%	1 mg
Sample No. 2	34%	93%	85%	69%	9 mg

The iron oxide is given in weight because it is present in the original composition only as an impurity of unknown concentration.

The magnesium and zinc were fairly effectively removed by this treatment. Only small amounts were found in subsequent analyses of the solid residue.

The treatment with sulfuric acid was fairly successful in leaving the manganese and phosphorus untouched. The use of cold instead of hot acid might have been better yet in order not to attack the manganese.

The treatment with nitric acid (Sample No. 2) was obviously unsuccessful as it dissolved far too much manganese and phosphorus.

The purpose of the next step was to remove the manganese. Each sample was warmed for about 45 minutes at about 60°C in a dilute sulfuric and oxalic acid solution.

A slight excess of the necessary amount of oxalic acid was present in both samples. In the case of Sample No. 1, an insufficient amount of sulfuric acid was inadvertantly used, and as a result the manganese was not well dissolved. After filtration the filtrate showed the following percentage amount of the substance assumed initially present.

	MnO_2	Mg	ZnO	Fe_2O_3
Sample No. 1	20%	3%	1%	10 mg
Sample No. 2	4%	0%	0%	6 mg

An analysis for phosphorus was not made.

It can be seen that this experiment was not a good test of the use of oxalic acid to dissolve manganese because of the procedural error with Sample No. 1, and because there was not much manganese present at the start in Sample No. 2.

As a third and final extraction, the residues from the previous step were heated 30 minutes at 100°C with excess concentrated hydrochloric acid. They were filtered and the filtrate contained the following percentage of the assumed original composition:

	MnO_2	Mg	ZnO	Fe_2O_3
Sample No. 1	35.5%	0%	6%	13 mg
Sample No. 2	0.0%	0%	0%	2 mg

This step was apparently effective in removing the remaining manganese, as no significant amount was detected later. However, if the extraction with oxalic and sulfuric acids had been carried out properly it would have probably removed most of the manganese and iron, and an extraction with hydrochloric acid would be unnecessary.

The reddish residues from the last filtration were washed, dried and weighed. Residue No. 1 was heated in a covered crucible. The weight loss, assumed to be elemental phosphorus

amounted to 2.4g which equals 89% of the assumed initial amount of phosphorus. 0.22g of an acid-insoluble residue was not analyzed but was possibly composed of phosphates of metals not extracted earlier.

The residue from No. 2 was not analyzed, but it was probably red phosphorus fairly free from metal. Its weight corresponded to 61% of the initial phosphorus of the sample.

The total amount of materials accounted for in all the procedures were:

	P	MnO_2	Mg	ZnO	Fe_2O_3
Sample No. 1	89%	63.5%	95%	70%	24 mg
Sample No. 2	95%	97%	85%	69%	17 mg

The differences from 100% are a bit large in a few cases, and must be ascribed to inexperience in handling and analyzing the materials.

A two-step process would probably effect the desired separation. The magnesium and zinc oxide would first be removed with cold dilute sulfuric acid. The manganese dioxide and iron oxide would be removed with a warm mixture of dilute sulfuric and oxalic acids. The residue should be fairly pure red phosphorus. The filtrates from the two extractions could be precipitated with alkali or carbonate to recover the metals as oxides, hydroxides, or carbonate.

While the procedure would be relatively simple and effective it has a severe disadvantage in the high cost of the oxalic acid needed. A cost comparison with other methods will be given later.

Extraction with Hydrochloric Acid

The basic reaction here is the reduction of manganese dioxide and the oxidation of chloride to chlorine gas:

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2\uparrow + 2H_2O .$$

Since the hydrochloric acid also attacks magnesium and zinc oxide, and to some extent iron oxide, red phosphorus of reasonable purity should be recovered. As with the oxalic acid method, a preliminary separation of the magnesium and zinc should be possible using cold, dilute sulfuric acid. In one trial a weighed 5.5g sample was heated with excess concentrated HCl. The addition of oxalic acid after cooling produced no further reaction. The sample was filtered. The dried residue amounted to 49.5% of the original sample. Its composition was not determined, but the weight is consistent with a loss of all of the metals and metal oxides and 7% of the phosphorus.

The use of hydrochloric acid was abandoned because of the inevitable production of large amounts of chlorine gas, which is noxious and corrosive. To operate the process efficiently and safely would require a sizeable capital equipment investment.

DIFFERENTIAL SETTLING RATES

The goal of this method was to separate the ingredients of the red phosphorus smoke composition from a liquid medium based on the differences in density and particle size of the ingredients.

These properties are as follows for the various ingredients:

	P	MnO_2	Mg	ZnO
Specific Gravity	2.2	5.0	1.7	5.5
Particle Size (μ)	5-25	75(avg)	125-175	<88
Reference	(4,5)	(6)	(7)	(8)

A number of experiments were performed where approximately five grams of red phosphorus smoke composition were placed in a two-liter beaker with one liter of water as the flotation medium. The suspension was stirred at high velocity with a magnetic stirrer for 15 minutes. The rotational force of the magnetic stirrer broke up the lumps of smoke composition and suspended approximately 95% of the particles. The suspended particles were then decanted and the experiment was repeated several times with the particles which had settled until they were predominately black instead of red. The decanted material was inspected under the microscope. There appeared to be about 1-3 percent of pyrolusite and zinc oxide in the material.

In several experiments it was shown that the decanted suspensions could be centrifuged and that the sediments settled into recognizable bands, though the separation achieved this way was not sharp.

In spite of the rather incomplete separation based on differential settling rates, this inexpensive process could have value as a first step in a total separation scheme.

SUBLIMATION

The goal of this method was to sublime the red phosphorus out of the composition directly.

In order to avoid igniting the composition it must be sublimed at reduced pressure or in an inert atmosphere. Data in reference 9 indicates that a sublimation pressure of 76 mm Hg is achieved at 300°C, and a pressure of 1-3 mm Hg at about 200°C.

A sublimator was fabricated with a "cold finger" trap to condense the sublimate of red phosphorus. Two trials were made, one at 1 torr pressure and one in a nitrogen atmosphere at ambient pressure. In both cases, sufficient oxygen was present from MnO_2 dissociation to cause some oxidation of the phosphorus. In addition, much of the condensed phosphorus was of the white form.

This method was then abandoned because of the safety and engineering problems of handling white phosphorus and because of the anticipated capital equipment cost of operation at high temperature and/or under partial vacuum.

INCINERATION CONCEPT EVALUATION BY BATTELLE

Subsequent to the work described in the previous section, Battelle was requested to evaluate the process concept and proposed equipment design concepts. The following is quoted directly from the Battelle report.

NAD Crane has developed a process concept for the demilitarization of a pyrotechnic munition used as a location marker. The concept involves burning the red phosphorus contained in the pyrotechnic composition to reclaim a phosphoric acid product for fertilizer application. As part of the overall development efforts by NAD Crane, Battelle was requested to review a process and equipment design concept developed by NAD Crane by conducting an experimental combustion study and a state-of-the-art review of applicable technology and process equipment.

The findings from this study indicate that the overall process concept developed by NAD Crane appears technically sound and feasible for the reclamation of a fertilizer-grade phosphoric acid from the red phosphorus composition. Other conclusions drawn from this study with respect to individual process steps indicated in the NAD Crane equipment design concept are listed below.

1. An incinerator design, based on the utilization of two combustion chambers as indicated in the NAD Crane design concept, appears to be the preferred approach in providing a flexibility in incinerator operation required to achieve complete combustion of red phosphorus. A low-sulfur distillate fuel, such as No. 2 fuel oil, would be satisfactory for incinerator operation.

2. A heat exchanger and a fabric filter included in the NAD Crane equipment design concept for removing entrained ash particles from the gaseous combustion products would appear to be neither workable nor necessary.

3. A combination of an orifice scrubber and a mist eliminator as indicated in the NAD Crane equipment design concept seems to be practical and feasible to achieve efficient recovery of a phosphoric acid product and to minimize stack gas emissions of phosphoric acid mist.

4. A phosphoric acid product recovered from the wet scrubber and the mist eliminator would be suitable for use in the manufacture of a solid fertilizer, such as triple superphosphate, without purification of the product.

The results of this study can be utilized by NAD Crane to proceed with the design of a pilot plant to demonstrate the feasibility of the process concept and to obtain design data for a full-scale system.

INCINERATION OF RED PHOSPHORUS

The purpose of this method was to incinerate the phosphorus smoke composition and recover the phosphorus pentoxide smoke as phosphoric acid solution.

Procedure

A number of experiments were performed in which a few grams of the phosphorus composition were burned inside a glass tube in a stream of air. The composition was spread out and ignited at the downstream end to cause the burning to take place slowly. The smoke deposited in the cooler downstream portions of the burning tube and in columns of water through which it was bubbled. When spontaneous burning was complete, the tube was flamed with a gas burner to drive off more of the phosphorus pentoxide.

The slag was scraped from the tube, sometimes with the aid of water or acid, and saved for analysis. Contact with water usually produced bubbling and the odor of phosphine. In several cases, the slag was stirred and/or boiled with water to attempt to extract a part of the phosphorus pentoxide, hopefully without too much metal. The remainder was not very soluble in any acid tried, but was rendered soluble by fusion with potassium carbonate for the purpose of later analysis.

The individual experiments and the results of the analyses are given below. In only two cases were both the slag and the smoke analyzed completely. It will be noticed that there were sometimes serious discrepancies between the totals accounted for and the amount of ingredients assumed present initially. A lot of the differences must have been due to the handling problems and experimentation with the analytical methods. In one experiment a procedural error resulted in spillage of some of the scrubbing water. The resulting loss of phosphorus had to be estimated.

Run Number 1

In the first experiment 4.2g of composition were burned. The downstream portion of the burning tube and the two columns of scrubbing water were analyzed separately. The slag was not extracted with water. Considerable phosphorus pentoxide may have been lost by the prolonged baking out of each acid used in an attempt to dissolve the slag for analysis. The results based on the amount of each ingredient assumed present initially are:

	P	MnO_2	Mg	ZnO
Burning Tube	6.1%	0%	0.3%	1.0%
Scrubbing Column #1	5.6%	0%	0.3%	0.3%
Scrubbing Column #2	0.0%	0%	0.3%	0.0%
Slag	33.5%	65%	90.0%	62.0%
Total accounted for	45.0%	65%	91.0%	63.0%

The unaccounted for phosphorus in the analysis is probably in the slag, and is lost by prolonged baking during analysis. The 12% recovery of phosphorus in the smoke (6.1 plus 5.6) was the lowest of the three experiments analyzed and was probably due to insufficient flaming of the slag.

Most of the unaccounted for manganese and zinc were probably in the slag also. The loss is assumed due to excessive handling and errors in spectroscopic analysis.

Comparing the results of scrubbing column no. 1 and scrubbing column no. 2 it is doubtful that a significant quantity of smoke escaped the scrubbing columns. We see also that the smoke is fairly free of metal, even in the burning tube, where the deposit was just downstream from the flame.

Run Number 2

Because the previous run indicated that a large proportion of the phosphorus remained in the slag, we performed a second experiment to better analyze the slag. For this reason, the smoke was not caught. An initial 4.5g of composition yielded 4.4g of slag versus an expected amount of 1.9g if all of the phosphorus pentoxide had been driven off. The slag was extracted with hot water. The results were

	P	MnO_2	Mg	ZnO
Water extract	5%	9.0%	44%	8.0%
Remainder of slag		64.5%	52%	59.5%
Total in slag		75.5%	96%	67.5%

If it were assumed that all of the metals remained in the slag, it can be calculated from the initial and final weights that 50% of the original phosphorus also remained there, presumably as metal phosphates plus dissolved phosphorus pentoxide. We see that a tenth of this (5%) was in water soluble form.

Although the smoke was not caught and analyzed, we assume on the basis of the previous experiment that the unaccounted for manganese dioxide and zinc oxide were not in the smoke but were lost during analysis of the slag.

Run Number 3

To attempt to drive off the maximum amount of phosphorus pentoxide we burned 1.32g of composition. The flaming out was more intense than for any of the others. Two gas burners were directed at opposite sides of the tube until no more white smoke was produced. An appreciable amount of smoke was seen to escape at the end of the second scrubbing column. Taking this into account this experiment yielded the highest recovery. The slag was not analyzed because we were primarily interested in the efficiency of phosphorus recovery. The results were:

	P	MnO_2	Mg	ZnO
Burning Tube	10.5%			
Scrubbing Column #1	14.0%	0.1%	0.9%	1.5%
Scrubbing Column #2	9.5%			
TOTAL	34.0%			

About three times as much phosphorus was recovered as in the first experiment, and it had only a low contamination with metals. A comparison of the amount of phosphorus found in the two scrubbing columns increases our suspicion that a significant amount of phosphorus pentoxide escaped the scrubbing columns, and thus the recovery figure could have been considerably higher.

Run Number 4

We wanted to confirm our observations about percent phosphorus recovery, and prove that a complete scrubbing of the smoke is possible. Therefore, in a final experiment of this type, 1.30g of composition were burned and the smoke passed through four columns of scrubbing water in series. Very little smoke was seen beyond the second scrubbing column, hence, the water from the last two scrubbing columns was not analyzed.

The slag was well flamed out, but not quite as intensively as in the previous experiment. It was then extracted by vigorous stirring in cold water. A partial loss of scrubbing water occurred on disconnecting the apparatus, which had to be estimated. The analytical results were:

	P	MnO_2	Mg	ZnO
Slag, extract	19.5%	12.5%	47%	15.5%
Slag, residue	25.0%	78.5%	77%	77.0%
Smoke burner and Scrub water combined	22.0%	0	1%	3.0%
TOTAL	66.5%	90.5%	125%	95.5%

The analytical results were of acceptable accuracy except for phosphorus. The unaccounted for phosphorus is 33.5% which equals to 0.18g, which would form 130 cc of phosphine gas at STP. It did not seem from the amount of bubbling which occurred when the slag was wetted that this much phosphine was formed, though it is conceivable. The phosphorus recovery in the smoke was lower than in the last experiment, though again it was not contaminated much with metals. A large amount of the phosphorus which remained in the slag was in water soluble form, though highly contaminated with the metal compounds.

Summary

Summarizing, the recovery of phosphorus in the smoke ranged from 12% to perhaps 40%. Contamination of the smoke with metals was less than 2% in all cases. Traces of elemental phosphorus were sometimes present as evidenced by a reddish color. This was minimized by the slowness of burning, and a

good air supply. Most of the elemental phosphorus was deposited just beyond the area of the burn and was removed by the flaming out.

The attempts to extract slag with water were unsuccessful in that contamination of the dissolved phosphorus pentoxide by metals was severe.

Slag Simulation Experiment

The amount of phosphorus pentoxide which remained in the slag in spite of intense flaming in the experiments just described was surprising. It was generally well in excess of the amount required to convert all of the metal oxides to phosphates. It is probably due to simple solution. To verify this, an experiment was performed in which 3.7g of phosphorus pentoxide was added to 1.30g of a mixture of manganese, magnesium, and zinc phosphates. The melting point of the mixture (synthesized to simulate slag) was sufficiently lowered that a liquid was obtained on heating with a gas flame in a covered crucible. The phosphates alone without the added phosphorus pentoxide could not be melted.

The liquid was heated to bright redness for 10 minutes until bubbling nearly stopped. The weight loss showed that 1.9g of the excess phosphorus pentoxide remained. The ratio of this to the original phosphates is considerably larger than the ratio of excess phosphorus pentoxide to phosphate left in the slag of the previous experiment. But it confirms the belief that an excess of phosphorus pentoxide can be physically dissolved in the phosphate involved in our system and that it is difficult to drive off with heat.

Wrapped Composition Experiment

An experiment of a different type was performed to examine the results of burning tightly packed composition inside a container. This was to simulate the results of incinerating smoke comp in the case. Heavy aluminum foil (3 mil) was rolled into hollow cylinders the size and shape of cigarettes. These were filled with loose composition packed in by hand using a glass stirring rod. Eight such units were stacked with random orientation into a can. Wide slits were cut into the sides of the can for ventilation and the can was placed in a fume hood with a strong forced draft. The pile was ignited by directing a large gas flame from the top for about a minute. The resulting burn was vigorous, though without loss of slag.

The can and contents were then partially immersed in cold water. Vigorous bubbling ensued, followed by ignition and a loud report in the space above the can. This was assumed to be due to ignition of phosphine gas formed from metal phosphide and water. The metal phosphides were evidence of oxygen deficiency within the tubes during combustion. No analysis was conducted on the smoke or the slag. The most important result was the oxygen starvation which can occur within a pile of units even with a draft directed at the outside of the pile, and the resulting hazard from formation of phosphides.

Observations

The experiments point to several problems which must be considered in designing or selecting the incinerator.

1. With the burning conditions and configuration used, the practical limit of recovery of the phosphorus is about 40%.

2. Much of the phosphorus pentoxide which is driven off settles out on cold surfaces immediately beyond the burning chamber.

3. The fine particles of phosphorus pentoxide require a much longer length of bubbling column (about six feet) for effective scrubbing than had been expected beforehand, and thus the scrubbing apparatus must be well designed.

4. Adequate air must be furnished to the burning system as a whole, otherwise a large amount of elemental phosphorus distills to the scrubber.

5. Where air cannot be blown directly over the burning surface, a large amount of metal phosphides are formed which are hazardous for later handling.

6. Finally, due regard must be given to the corrosive properties of phosphorus pentoxide, which is an acid, at high temperatures.

COST ANALYSIS AND CONCLUSIONS

A comparison of estimated operation costs (not including capital equipment) of the three methods most thoroughly investigated is shown in Table I. These methods are (a) incineration, (b) total digestion in hot nitric acid, and (c) separation by extraction with sulfuric and oxalic acids.

The cost estimates indicate that the incineration method will result in considerable saving of labor if it proves unnecessary to crush the composition out of the thin metal case before incineration.

From a material standpoint the three methods are nearly equal. The acid methods produce more valuable products, but this is balanced by the cost of the acid required. Most of the material cost of the sulfuric-oxalic acid method is for the oxalic acid.

The material recovery figures for this method include only the phosphorus and exclude the manganese recovered.

The materials cost estimate for the nitric acid method does not include the cost of removing the manganese from the phosphate solution. Without this separation, the resulting phosphate fertilizer would be restricted to use in non-acid soils, pH $\geq$ 5.5 in order to avoid manganese toxicity, reference 10. Yearly soil sampling would continue to be required.

CONCLUSIONS

Three methods of recovering phosphorus from red phosphorus pyrotechnic smoke composition were investigated in some detail. These were:

1. incineration,

2. extraction with sulfuric-oxalic acids,

3. total oxidation with nitric acid.

TABLE I

COST ANALYSIS PER 100 POUNDS COMPOSITION

Operation	Incineration	Total Digestion Nitric Acid	Acid Extraction Sulfuric-Oxalic
1. Receive, Breakdown, Recover Candles	$47.00	$47.00	$47.00
2. Remove Candle Case, Granulate Composition	--	$40.00	$40.00
3. Operating Costs Labor, Utilities, etc.	$31.50	$28.60	$28.60
4. Material Cost Acids	--	$29.00	$49.00
Sub Totals	$78.50	$144.60	$162.60
5. Returns	*Acid $17.00	Metal Phosphate Solution $37.40	Red Phosphorus $47.83
6. Net Cost	**($61.50)	($107.20)	($114.67)

*Assumes 40% of the red phosphorus is recovered as phosphoric acid, and commercial fertilizer costs of $199/ton and $175/ton for phosphorus and nitrogen fertilizers

**Net costs in the parentheses represent the investment required to process 100 pounds of composition

The incineration method was concluded to be the most desirable because the operational cost of this method is estimated to be less than the other two methods above. Continued study of the incineration method is recommended to provide the data necessary for a pilot plant design.

Two additional methods were investigated briefly: reduction and separation of the metallic components with hydrochloric acid, and gravitational separation.

The hydrochloric acid method initially appeared attractive because it would enable elemental red phosphorus to be reclaimed for sale or reuse. However, the potentially large capital investment and the hazards involved with the handling of chlorine gas, librated during the process, were the reason for removal of this process from further consideration.

The gravitational method was found to give insufficient separation by itself, though it could be useful as part of a total process.

REFERENCES

1. D. M. Johnson and C. W. Gilliam, *Pollution Abatement: Reclamation of Red Phosphorus Smoke Composition*, RDTR No. 267, Naval Ammunition Depot, Crane, Indiana (1 April 1974), AD 778 341.

2. Eldon L. Hood, *Evaluating a Magnesium Ammonium Phosphate Suspension as a Fertilizer Material*, RDTR No. 283, prepared by the Department of Agronomy, Purdue University, West Lafayette, Indiana for the Naval Ammunition Depot, Crane, Indiana (12 December 1974), pp. 1-6 and 16-25.

3. K. L. Wagaman and T. J. Sullivan, *Industrial Preparedness Measure: Propellant Disposal/Reclamation Facility Design*, IHMR 73-240, Naval Ordnance Station, Indian Head, Maryland (28 September 1973), p. 5.

4. W. Ripley, *A Preliminary Investigation of the Reactivity of Amorphus Red Phosphorus*, RDTR No. 110, Naval Ammunition Depot, Crane, Indiana (March 1968), pp. 27-28, AD 832 086.

5. Red Phosphorus Specification, MIL-P-211, Class 2.

6. Manganese Dioxide Specification, MIL-M-3281, Grade B, Class 1 or 2.

7. Magnesium Powder Specification, MIL-M-382, Type I, Grade A, Gran 6.

8. Zinc Oxide Specification, MIL-Z-291, Grade 1.

9. J. W. Mellor, *Inorganic and Theoretical Chemistry* (Wiley Interscience Publishers, New York, 1971), Vol. VIII, Supplement III, p. 156-9, Table VI.

10. Manganese, National Research Council, Washington, D. C. (January 1974), PB-232 663, Available from NTIS, p. 54.

APPENDIX A

PHOSPHORUS DEVICE INVENTORY SPCC SEARCH 14 APRIL 1975

Nomenclature	DOD Code	Units Codes* A,B&C	Units All** Other Codes	Wt/Unit	Comp/Unit	Unit*** Gross Wt	Comp*** Gross Wt
Marker, Marine, Location, Mk 25-2&3	L554	257,318	23,939	3.74#	1.02#	89,532	24,418
Signal, Smoke & Illumination, Aircraft, Mk 6-2&3	L525	3,659	8,714	15.08#	4.00#	131,407	34,856
Marker, Marine, Location, Mk 26-0	L578	218	144	3.30#	0.60#	475	86
Marker, Marine, Location, Mk 27-0	L579	1,939	1,711	3.40#	0.60#	5,817	1,020
Marker, Marine, Location, Mk 9-0	L572	0	0	3.50#	1.02#	0	0
Marker, Marine, Location, Mk 58-0	L585	21,821	53,424	12.90#	4.73#	689,170	252,700
Signal, Smoke & Illumination, Aircraft, Mk 5-3&4	L292	95	2,681	3.60#	1.02#	9,652	2,735
Marker, Marine, Location, Mk 75-0	L587	40	0	7.00#	0.64#	0	0
Cartridge, Signal, Practice Bomb, Mk 4-0, 1&3	F562	634,336	74,515	0.20#	0.06#	14,903	4,471
Cartridge, Signal, Practice Bomb, Mk 4-2&4	F563	0	0	3.40#	1.02#	0	0
Signal, Marine, Smoke & Illumination, Mk 55-0	UW79	0	0	4.44#	1.34#	0	0
TOTALS		919,426	165,127			940,956	320,286
TOTAL TONS						470	160

Footnotes on next page

FOOTNOTES FOR APPENDIX A

*Condition Codes are required to segment and identify the physical condition of ammunition material. Codes A, signifies a serviceable material which can be issued without qualification, Code B is a serviceable material to be issued with qualification, and Code C is a serviceable item, issuable under priority and takes precedence over Codes A & B.

**All other codes include D, E, F, G. H, J, K, L, M, and N which are unserviceable and suspended items for one reason or another.

***These two columns refer.to unserviceable items destined for disposal.

APPENDIX B

COMBUSTION PRODUCT PROPERTIES

	mp(C)	bp(C)	Decomposition
Mn_3O_4	1,705		
MnO_2 di	-0, 535		
MnO mono			
$Mn_2P_2O_7$ pyro	1,196		at 750 stable for short periods or longer. at 1050 slowly loses 1/3 of the P_2O_5
MnP	1,190		
Mn_3P_2	1,095		
MgO	2,800		
$Mg_3(PO_4)_2$ ortho	1,184		
Mg_3P_2			
$Mg_2P_2O_7$			at 1200 slowly decomposes
ZnO	1,975		
$Zn_3(PO_4)_2$ ortho	900		
$Zn_2P_2O_7$ pyro			
Zn_3P_2	420	sublimes 1100	
P_2O_5	580	sublimes 300	at 1700, 50% to P_2O_3 at equil.
P_2O_3		sublimes 174	